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Investigation of Analyzer Problems in the Measurement of NOx from Methanol Vehicles

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INVESTIGATION OF ANALYZER PROBLEMS IN THE MEASUREMENT OF NOx FROM METHANOL VEHICLES

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ABSTRACT

This study was conducted to investigate the extent and source of irregularities related to the measurement of NOx emissions from methanol cars. Corrective measures were also explored.

It was observed that NOx chemiluminescent analyzers respond to methanol and formaldehyde after being exposed to high concentrations of methanol and formaldehyde over extended periods. This response can cause significant errors in the measurement of NOx from methanol cars which have inherently elevated concentrations of exhaust methanol and formaldehyde. The most effective way of eliminating the spurious response is to clean the analyzer's reaction chamber regularly when testing vehicles which are being operated on methanol fuels.

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SECTION I

INTRODUCTION

The rapid development of vehicles designed to operate on methanol fuel has prompted development and evaluation of methods for measuring their emissions. Classical measurement methods prescribed for gasoline cars are not always applicable to methanol cars because of the inherently high concentrations of methanol and formaldehyde in their emissions. One such exception applies to the FID (flame ionization detector) measurement of hydrocarbons in the presence of methanol (1,2,3). Another less publicized exception and the subject of this report pertains to the chemiluminescent method of measuring nitrogen oxides (NO_x) from methanol cars.

The chemiluminescent method is based upon the principle that nitric oxide (NO) can be reacted with ozone (O_3) to give about 10 percent electronically excited NO_2*. When the electronically excited NO_2* transits to its normal state, a detectable light emission is given off. The intensity of this emission is directly proportional to the mass flow rate of NO into the reaction chamber. The light emission is detected and measured by a photomultiplier tube and the associated electronics process a voltage response which is proportional to the intensity of light being emitted. To make this method applicable to NOx (NO + NO_2) emissions, the NO_2 in the sample is changed to NO in an NO_2 converter (4).

Problems with chemiluminescent NO_x measurement from methanol cars were first reported as large variations in NO_x data and large values of NO_2 (5). Later descriptions identified a sort of residual response which occurred immediately following sample analysis while the analyzer was being zeroed.

These symptoms were observed with older analyzers which had been exposed to high formaldehyde and methanol emissions from methanol cars. Because the above symptoms had not been observed on newer analyzers, an interference problem caused by contamination of some sort was suspected.

This study was undertaken to determine (1) the source of irregularities associated with the chemiluminescent measurement of NO_x emissions from methanol cars, (2) the severity of the measurement problem, and (3) any corrective action which might be taken. One of the older analyzers which was known to have the problem and a brand new analyzer on loan from the manufacturer were available for the study. Both were Beckman 951A Chemiluminescent NO_x Analyzers.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

A study was carried out to investigate the extent and source of irregularities related to the measurement of NOx emissions from methanol cars. Corrective measures were also explored. Because the results in this study were obtained in tests using Beckman 951A Chemiluminescent Analyzers, some of the conclusions based on those results are relative to the experience with that particular analyzer. However, there is evidence which suggests that other types of chemiluminescent analyzers could be similarly affected.

The conclusions of the study are as follow:

1. NOx chemiluminescent analyzers respond to formaldehyde and methanol gases when exposed to high concentrations of these gases over extended time periods.

2. The response to formaldehyde and methanol can be severe enough to cause significant errors in the measurement of NOx emissions from methanol cars.

3. Analyzer response to methanol accounts for most of the error when measuring NOx emissions from methanol cars.

4. Reactions involving formaldehyde in the reaction chamber are the principal cause of spurious analyzer response with samples containing either methanol or formaldehyde.

5. The most effective way of eliminating the spurious response is to clean the reaction chamber in accordance with the manufacturer's instructions.

Further research is recommended to definitively identify the wavelengths of light emission associated with the interference. Bracketing the range of those wavelengths might be accomplished through an examination of the effect of different cut-off filters on response to formaldehyde. Such an approach might lead to the selection of an improved filter which could eliminate the interference altogether.

It is also recommended that a study be carried out on other chemiluminescent analyzers to determine the effect of long term exposure to high concentrations of methanol and formaldehyde. Thus far only the Beckman 951A models have been so exposed as a result of emission tests on malfunctioning methanol cars. Until such studies are completed, one must assume that all NOx chemiluminescent analyzers could develop problems associated with extended testing on methanol cars. Therefore, when testing methanol cars, more than the usual care should be taken by instrument operators to assure that their instruments are clean and well maintained.

SECTION 3

EXPERIMENTAL PROCEDURES

Upon arrival of the two analyzers involved in the study, a series of routine checks were completed to assure that instrument performance was within the manufacturer's specifications. Emphasis was placed on linearity, stability, and precision. One of the analyzers was new; the other had been in service for over two years at EPA, Office of Mobile Sources, Ann Arbor, Michigan. Residual response and large variations in the measurement of NO_x from methanol cars had been exhibited by the older analyzer, but both analyzers appeared to be operating in accordance with design specifications.

In order to test for and determine the extent of a suspected interference problem with formaldehyde and methanol, samples were prepared in the following manner: Measured quantities of liquid formalin solution (37% formaldehyde by weight) and methanol were injected through a syringe into a heated (100°C) reaction chamber. The chamber was swept with zero air flowing at a rate of 5.7 ℓ/m over 10 minute time intervals. The formaldehyde and methanol gases exiting the reaction chamber were introduced into a Tedlar bag which was sampled by the analyzers shortly after its preparation.

Some samples were generated using the tailpipe emissions from a 1983 Methanol Escort. The Methanol Escort was being operated on M85 fuel (85% methanol, 15% gasoline) and its tailpipe emissions were controlled by a three-way, air-injected catalyst. Analyses of the samples from Bag 1 (cold transient test phase) of the Federal Test Procedure (FTP) were run because

this test phase contains the highest levels of methanol and formaldehyde. NO_x emissions were measured with a TECO chemiluminescent analyzer for comparison with measurements made using the older Beckman 951A. During these experiments, both analyzers were zeroed and spanned using the same gas cylinders.

Troubleshooting the contamination problem on the older Beckman analyzer was carried out by systematically exchanging parts from that analyzer with parts from the uncontaminated new Beckman. The entire photomultiplier tube-reaction chamber unit was first exchanged, then components within that unit including the red filters, photomultiplier tubes, and reaction chambers were individually switched out. After each exchange, the analyzers were rechecked for zero and span stability, and for response to formaldehyde or methanol. Frequent linearity checks were made using a flow divider in conjunction with the span gas.

At one point in the study, a catalyst was devised to scrub the formaldehyde and methanol at the sample inlet to the analyzer. The catalyst was 0.5% rhodium on alumina substrate, occupied a volume of about 50ml, and had a surface area of 200 m^2/g. Temperature of the catalyst was controlled by varying the current flow through heat tape which had been applied to a glass tube containing the catalyst material.

Cleaning of the reaction chamber in the older Beckman analyzer was done by scrubbing with Alconox in deionized water, then by soaking the chamber in 50 percent concentrated HCl for five minutes, followed by a thorough rinse with deionized water. These cleansing techniques were done in accordance with procedures given in the instrument manual.

SECTION 4

RESULTS AND DISCUSSION

Two Beckman 951A Chemiluminescent NO_x Analyzers were involved in this study. One had been used in testing by EPA, Ann Arbor, the other was a new instrument on loan from Beckman Industrial. The instrument from Ann Arbor had been in service for over two years and was exhibiting symptoms of high measurement variability and residual response to methanol car emissions. During preliminary tests performed in Ann Arbor, analyzer response to formaldehyde was observed.

Following delivery and check out of the older instrument, tests were conducted to determine the extent of the reported formaldehyde interference. The results of these tests are given in Table 1. Response to formaldehyde tends to increase more rapidly at the lower formaldehyde concentrations, then tails off at levels above 150 ppm. Response was greater when the analyzer was being operated in the NO mode (converter by-pass) and was greater in both NO and NO_x modes as ozone pressure was reduced from 30 psi to 5 psi. For these tests the converter temperature was maintained at 220°C, its optimum for NO_2 to NO conversion.

Tests were also run on the older analyzer to determine if it responded to methanol. After obtaining an appreciable response to a 250 ppm methanol sample, responses to lower methanol concentrations were measured with the results given in Table 2. Although the analyzer responded less to methanol than formaldehyde, NO_x measurement irregularities experienced with this

analyzer were probably more influenced by methanol emissions because these greatly exceed those of formaldehdye from methanol cars.

When the analyzer was operated in the NO mode (sample is by-passed around a NO_2 to NO converter), response to methanol decreased sharply (see Table 2). This was opposite the experience with formaldehyde where the sample bypassed around the converter resulted in a greater response. These results suggest that methanol could be reacting in the converter to form formaldehyde which ultimately causes the response. There is a very strong likelihood of this occurrence because the converter had been optimized and was operating at a relatively cool 220°C, a temperature highly conducive to the conversion of methanol to formaldehyde. Commercial production of formaldehyde takes place through low temperature conversion of methanol over a catalyst.

A preliminary measure taken to remedy the interference problem was to combust the formaldehyde and methanol by increasing the converter's temperature. As converter temperature was increased, response to both formaldehyde and methanol decreased until essentially no response was detected at 400°C. For the remedy to work the tests had to be run in the NO_x mode with the sample passing through the converter; therefore, interference in the NO mode (converter by-pass) remained unimproved. In addition to this drawback, the heightened converter temperatures resulted in lowered NO_2 to NO conversion efficiencies. This was undesirable because analyzer performance was being severly compromised.

Use of a catalyst (rhodium on alumina) for scrubbing out methanol and formaldehyde in the sample gas to the analyzer was also examined. At elevated

temperatures the catalyst was effective in oxidizing both methanol and formaldehyde and in eliminating the interference problem; however, it was also effective in reducing the NO in nitrogen used to span the analyzer. When catalyst temperature was reduced to ambient levels the span problem was eliminated and both methanol and formaldehyde were being sufficiently scrubbed. But after prolonged catalyst usage, instrument zero began to drift upwards suggesting gradual elution of formaldehyde.

The new 951A analyzer from Beckman arrived during the time that the catalyst scrubber for the old analyzer was being evaluated. The new analyzer did not respond to either formaldehyde (100 ppm) or methanol (250 ppm). This finding was consistent with reports indicating that the interference problem appeared only in analyzers which had been exposed to high concentrations of methanol car exhaust for extended periods. Because the new analyzer did not respond to formaldehyde, the task of isolating the component on the older analyzer responsible for response became simplified. By systematically exchanging parts between the two analyzers, the responsible component was found to be the reaction chamber. After the reaction chamber was cleaned, reassembled, and tested, response to formaldehyde (100 ppm) and methanol (250 ppm) was less than 2 ppm.

NO_x measurements were made on tailpipe emissions from a Methanol Escort with the older Beckman 951A before and after its reaction chamber was cleaned.

Emissions from Bag 1 of the FTP were measured because these contain relatively high levels of methanol and formaldehyde. In an earlier study on this vehicle (6), the Bag 1 methanol and formaldehyde concentrations were about 50 ppm and 3.5 ppm, respectively. FTP emissions results from this study are given in Table 3. Although the emission rates given for carbon monoxide and total organics (total hydrocarbons + methanol + formaldehyde) exceed the standard levels being promulgated for methanol cars (7), they are typical for an older car such as this one was.

NO_x measurements on Bag 1 were made using a TECO chemiluminescent analyzer for comparison with results from the older Beckman 951A. The TECO instrument had not been previously exposed to high concentrations of methanol car emissions and did not respond to high concentrations of methanol or formaldehyde. The results shown in Table 4 illustrate the effect of cleaning the reaction chamber on agreement between measurements made with the TECO and the older Beckman analyzer. Before cleaning, the Beckman measurement was about 35 percent higher than the measurement from the TECO. After cleaning, the difference between measurements was reduced to about 3 percent.

Toward the conclusion of the study, the new Beckman 951A began responding to formaldehyde. A response between 4 and 7 ppm was obtained with a 100 ppm formaldehyde sample. No response to methanol occurred. It is estimated that this first observed response to formaldehyde occurred after subjecting the new analyzer to three to four 60 liter bags of 100 ppm formaldehyde and two to three bags of 250 ppm methanol. Unfortunately, time restraints prohibited any further investigation of the effects of prolonged exposure to formaldehyde on analyzer performance.

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TABLE 1. ANALYZER RESPONSE TO FORMALDEHYDE

Formaldehyde Concentration (ppm)	RESPONSE			
	NOx Mode 30 psi O_3	NO Mode 30 psi O_3	NOx Mode 5 psi O_3	NO Mode 5 psi O_3
0	0.5	0.6	0.5	0.5
25	10.7	11.7	21.0	21.3
50	16.1	17.6	28.0	29.6
100	21.8	23.5	-	-
150	25.5	29.2	32.5	34.0
200	27.0	-	-	-

TABLE 2. ANALYZER RESPONSE TO METHANOL

Methanol Concentration (ppm)	RESPONSE			
	NOx Mode 30 psi O_3	NO Mode 30 psi O_3	NOx Mode 5 psi O_3	NO Mode 5 psi O_3
0	0.8	0.8	0.8	-
31	8.3	2.9	15.0	13.4
62	11.2	3.7	-	-
125	14.1	4.7	-	-

TABLE 3. FTP EMISSION RATES FOR THE METHANOL ESCORT

THC, g/mi	0.48
Methanol, g/mi	0.96
CO, g/mi	6.97
NO_x, g/mi	0.64
HCHO, mg/mi	122.30

TABLE 4. ANALYZER COMPARISON OF BAG 1 MEASUREMENTS OF METHANOL ESCORT NO_x EMISSIONS

TECO	BECKMAN 951A		
NOx Mode (ppm)	NOx Mode (ppm)	NO Mode (ppm)	% Diff NOx Mode
13.6	18.6*	14.5*	+ 36.8%
12.3	12.7**	-	+ 3.2%

* Before 951A was cleaned
** After 951A was cleaned